

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08G 18/28, 18/48, C09D 175/04, C08G 18/79		A1	(11) International Publication Number: WO 96/30425 (43) International Publication Date: 3 October 1996 (03.10.96)
(21) International Application Number: PCT/US96/01237 (22) International Filing Date: 31 January 1996 (31.01.96) (30) Priority Data: 08/411,253 27 March 1995 (27.03.95) US (71) Applicant: PPG INDUSTRIES, INC. [US/US]; One PPG Place, Pittsburgh, PA 15272 (US). (72) Inventors: MARTZ, Jonathan, T.; 2509 Hamilton Avenue, Glenshaw, PA 15116 (US). CARNEY, Joseph, M.; 404 Hoffman Road, Pittsburgh, PA 15212 (US). JENNINGS, Robert, E.; R.D.#2 Box 5270, Elwood City, PA 16117 (US). DONNELLY, Karen, D.; 2837 Anderson Drive, Allison Park, PA 15101 (US). (74) Agents: MILLMAN, Dennis, G.; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 (US) et al.		(81) Designated States: AU, BR, CA, JP, MX, SG, TR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.	

(54) Title: EMULSIFIERS AND THEIR USE IN WATER DISPERSIBLE POLYISOCYANATE COMPOSITIONS

(57) Abstract

An aqueous two-component polyisocyanate coating composition is based on an essentially isocyanate-free emulsifier that comprises the reaction product of: (i) an isocyanate and (ii) a member selected from the group consisting of: hydroxy functional polyalkyl ethers containing at least five ethylene oxide, alcohols different from said polyalkyl ethers, amine compounds, and combinations thereof. The hydroxy functional polyalkyl ether is provided in a quantity sufficient to react at least one equivalent of isocyanate groups in polyisocyanate (i), and the total amounts of reactants (ii) are sufficient to react all of the isocyanate groups of the polyisocyanate (i).

102/103

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

EMULSIFIERS AND THEIR USE IN WATER DISPERSIBLE POLYISOCYANATE COMPOSITIONS

Field of the Invention

5 This invention relates to emulsifiers, their preparation and use in water dispersible polyisocyanate compositions, and to aqueous, two-component coating compositions incorporating the water dispersible polyisocyanate compositions and emulsifiers in combination with an aqueous, polymeric resin having isocyanate-reactive groups.

10

Background of the Invention

 The use of water based coatings, as opposed to solvent based coatings, has become increasingly more important due to environmental considerations. However, in the case of isocyanate-reactive coatings, the presence of water presents a
15 problem in that the isocyanate groups react not only with the isocyanate-reactive groups with which they are intended to react, but also with the water as well. In order to overcome this disadvantage, the prior art has made use of emulsifiers that are the reaction product of polyisocyanates and hydroxy functional polyethers such that the emulsifier retains latent isocyanate functionality to assist in the crosslinking reaction
20 of the coating and sufficient hydrophilic character to keep the coating composition dispersed in an aqueous medium.

 U. S. Patent No. 3,996,154 discloses emulsion of an aromatic polyisocyanate in water using an isocyanate functional, non-ionic surface active agent containing oxyethylene groups. U. S. Patent No. 4,472,550 provides for similar
25 emulsions that are useful as binders, where the isocyanate functional emulsifier is based on a variety of polyisocyanates. U. S. Patent Nos. 4,663,337 and 5,296,160 disclose polyisocyanate compositions suitable for dispersion in water, which contain isocyanate functional emulsifiers. U.S. Patent No. 5,200,489 is directed to a polyisocyanate composition that is dispersible in water with an average isocyanate

functionality of 2 to 6 prepared by reacting a 1,6-hexamethylene diisocyanate based polyisocyanate adduct and an emulsifier based on the polyisocyanate adduct or another polyisocyanate and a monohydroxy functional polyether, such that the polyisocyanate composition in combination with an isocyanate-reactive aqueous polymer resin provides a coating composition. U.S. Patent No. 5,252,696 relates to the composition and preparation of water-dispersible polyisocyanate mixtures having an average isocyanate functionality of 1.8 to 4.2 and containing cycloaliphatically bound isocyanate and ethylene oxide groups.

The use of isocyanate functional materials often requires that precautions be taken with respect to handling and use based on sensitization and toxicity considerations. Such precautions can be relatively burdensome when the coating compositions are utilized under controlled factory conditions, for example, manufacturing of automobiles. Automotive refinishing coatings, however, tend to be applied under conditions that are not nearly as controlled as in automobile plants.

In addition, the synthesis and production of novel isocyanate compounds and compositions has come under strict regulation by governmental agencies, and therefore it is increasingly difficult to obtain clearance for manufacture of new materials, especially those that fall into the categories of compounds including isocyanates.

Therefore, there is a need for polyisocyanate based emulsifiers that contain substantially no isocyanate-reactive groups, preferably none, in order to readily disperse the aqueous, two-component, isocyanate-reactive coatings in water while maintaining the superior performance properties of these coatings. It would also be beneficial if a wide range of polyisocyanates could be employed in the preparation of the emulsifier.

Summary of the Invention

One aspect of the present invention is an emulsifier that comprises the reaction product of:

- (i) an isocyanate and

-3-

(ii) a member selected from the group consisting of hydroxy functional polyalkyl ethers containing at least five ethylene oxide, alcohols different from said polyalkyl ethers, amine compounds, and combinations thereof. The hydroxy functional polyalkyl ether is provided in a quantity sufficient to react at least one equivalent of isocyanate groups in polyisocyanate (i), and the total amounts of reactants (ii) are sufficient to react all of the isocyanate groups of the isocyanate (i), i.e., at least 99 percent of the isocyanate groups originally present in the isocyanate component (i). The isocyanate composition (i) is preferably a polyisocyanate.

The present invention is also includes an aqueous polyisocyanate composition, as well as an aqueous two-component coating. The polyisocyanate composition (I) comprises a polyisocyanate (a) and the substantially isocyanate-free emulsifier (b) described above, wherein that the emulsifier (b) is present in an amount of from 5 to 75, preferably 15 to 40, percent by weight based on the resin solids weight of (a) plus (b). The aqueous two-component coating composition comprises the polyisocyanate composition (I) and an aqueous polymer resin (II) that contains isocyanate-reactive groups, wherein the components (I) and (II) are present in an amount sufficient to provide an equivalent ratio of isocyanate groups to isocyanate-reactive groups of about 0.5:1 to 5:1, preferably 0.8:1 to 2:1. The isocyanate reactive groups are preferably hydroxyl groups and/or amine groups.

Detailed Description of the Invention

The emulsifiers of the present invention are the reaction product of an isocyanate and a hydroxy functional polyalkyl ether. Any organic isocyanate may be used, and suitable isocyanates would include known aliphatic, cycloaliphatic, aromatic and heterocyclic isocyanates. Examples of suitable isocyanates for preparing the emulsifier include phenyl isocyanate, octyl isocyanate, p-butyl phenyl isocyanate, o- and p-methoxy isocyanate, o-isocyanate benzyl chloride, cyclohexyl isocyanate, octyl isocyanate, octadecyl isocyanate, and chlorohexyl isocyanate. Preferred are polyisocyanates such as ethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate (HDI), 2,4,4-tri-methyl-1,6-hexamethylene diisocyanate,

1,12-dodecane diisocyanate, cyclobutane-1,3-diisocyanate, cyclohexane-1,3-diisocyanate, cyclohexane-1,4-diisocyanate, 1-isocyanato-2-isocyanatomethyl cyclopentane, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl cyclohexane (isophorone diisocyanate or IPDI), 2,4-hexahydrotolulene diisocyanate, 2,6-hexahydrotolulene diisocyanate, 2,4'-dicyclohexylhexylmethane diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, 2,4-tolulene diisocyanate (TDI), 2,6-tolulene diisocyanate, diphenyl methane-2,4'-diisocyanate, diphenyl methane-4,4'-diisocyanate (MDI), naphthalene-1,5-diisocyanate, triphenyl methane-4,4',4''-triisocyanate, polyphenylene

polyisocyanates and mixtures thereof. Also suitable are polyisocyanates containing carbodiimide groups, urethane groups, allophanate groups, isocyanurate groups, biuret groups, and urea groups. A particularly useful polyisocyanate for making the emulsifier of the present invention is the isocyanurate of isophorone diisocyanate.

The polyisocyanate is reacted with hydroxy functional polyalkyl ether which may be mono-, di- or tri-functional, although monohydroxy functional polyalkyl ethers are preferred. Examples of hydroxy functional polyalkyl ethers include glycol ethers that are made by reacting at least five moles of alkylene oxide groups with an alcohol. Examples of suitable hydroxy functional polyalkyl ethers include polyethylene glycol monomethyl ether, 1-isobutyl isopentyloxy poly(ethyleneoxy)ethanol, octylphenoxy poly(ethyleneoxy) ethanol, nonylphenoxy poly(ethyleneoxy) ethanol, and the like, including mixtures thereof.

In addition to the polyisocyanate and the hydroxy functional polyalkyl ether described above, an optional third reactant may be used to make the emulsifier of the present invention when polyisocyanates are used. This optional third ingredient preferably may be an alcohol, a glycol ether, an amine, or combinations thereof. These alcohols, glycol ethers and amines may be aliphatic, cycloaliphatic, or aromatic and may be primary or secondary. Suitable alcohols are those containing 1 to 12 carbon atoms, preferably 1 to 4 carbon atoms, such as, methanol, ethanol, propanol, butanol, cyclohexanol and phenol. Glycol ethers that are suitable as the optional third reactant are generally characterized by shorter alkylene oxide chain length (i.e., they

need not have at least five alkylene oxide groups) and include mono-, di- and, tri- and poly- ethylene and propylene glycol ethers, preferably ethylene glycol ethers, based on the isomers of methyl, ethyl, propyl, butyl and phenyl alcohols. Particular examples of the optional glycol ethers are ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol butyl ether, ethylene glycol hexyl ether, diethylene glycol methyl ether, diethylene glycol ethyl ether, diethylene glycol butyl ether, triethylene glycol methyl ether, triethylene glycol ethyl ether, triethylene glycol butyl ether, polyethylene glycol monomethyl ether, propylene glycol methyl ether, dipropylene glycol methyl ether, dipropylene glycol dimethyl ether, tripropylene glycol methyl ether, propylene glycol isobutyl ether, ethylene glycol phenyl ether, propylene glycol phenyl ether. Examples of amines useful as the optional third reactant include butyl amine, ethylene diamine, diethylene triamine, triethylene tetramine, 1,6-hexanediamine, piperazine, 2,5-dimethyl piperazine, 1,4-cyclohexanediamine, 1,2-propane diamine, hydrazine, methylamine, tetramethylenediamine, ethanolamine, diethanolamine, triethanolamine aniline, phenylenediamine, 2,4- and 2,6-toluyldiamine, polyphenylene polymethylene polyamines, and mixtures thereof. Other classes of compounds that may server as the optional third reactant include mercaptans, oximes, acetoacetates, sulfonate diols, and piperadines.

The emulsifier may be prepared by conventional polymerization techniques, either batch-wise by combining all of the ingredients, or step-wise by reacting the polyisocyanate and hydroxy functional polyalkyl ether, followed by addition of the optional alcohol, glycol ether and/or amine reactant. When the optional third reactants include an amine, it is preferred to add the amine after the polyisocyanate, hydroxy functional polyalkyl ether and any optional alcohol and/or glycol ether have been reacted. Typically the reaction mixture is heated to obtain a homogeneous mixture at temperatures of about 60°C to 80°C, preferably 70°C to 75°C, until infrared analysis indicates that no isocyanate functionality remains. Although, in principle, it is intended that all of the isocyanate functionality of the polyisocyanate be reacted, it should be understood that 100 percent complete reaction

cannot always be attained, and therefore, trace amounts of unreacted isocyanate should not be considered as being outside the scope of the present invention.

Alternatively, reacting "all" of the isocyanate for the purposes of the present invention may be defined as being at least 99 percent complete reaction, preferably 100 percent.

5 The resulting emulsifiers typically have a total solids content, based on total weight of the emulsifier composition, between about 65 to 100 percent. The number average molecular weight of the emulsifier of particular embodiments has been found to be between 1000 and 4000 as determined by gel permeation chromatography utilizing a polystyrene standard.

10 The emulsifier described above may be used to prepare a polyisocyanate composition by mixing the emulsifier with a polyisocyanate compound. Polyisocyanate compounds useful for inclusion in the polyisocyanate composition may be the same polyisocyanates previously mentioned in connection with the synthesis of the emulsifier. Polyisocyanates based on an isocyanurate or
15 biuret are preferred, with the isocyanurate of isophorone diisocyanate and the biuret of 1,6-hexamethylene diisocyanate being particularly useful examples. Typically, the polyisocyanate and emulsifier are blended with an organic solvent and agitated until a homogeneous solution is obtained. Suitable solvents are those that are not reactive with the polyisocyanate, such as ketones, acetates, and toluene. The polyisocyanate
20 composition may be comprised of 5 to 75 percent by weight of the emulsifier, preferably 15 to 40 percent, most preferably 25 to 35 percent, based on resin solids weights.

 The above polyisocyanate composition containing the emulsifier of the present invention may constitute one component of an aqueous two-component
25 coating composition. The other component of such a two-component coating comprises an aqueous or water dispersible resin that contains a polymer having isocyanate-reactive groups, for example hydroxyl groups and/or amine groups. The polymers that are useful for this purpose include those known in the art for use in isocyanate cured coatings. Examples of suitable polymers include hydroxyl
30 functional and/or amine functional acrylic polymers, polyester polymers, polyurethane

polymers, and polyaldimines. The aqueous polymer resin component may also contain optional ingredients and additives conventionally used in the coatings industry. Typical additives include solvents, pigments, catalysts, defoamers, thickeners, and surfactants.

5 Prior to application of the aqueous two-component coating composition, the polyisocyanate composition package may be added to the aqueous polymer resin package under slow and constant agitation. The two components may be combined in relative amounts sufficient to provide a ratio of isocyanate groups to isocyanate-reactive groups of 0.5:1 to 5:1, preferably 0.8:1 to 2:1. The aqueous two-
10 component coating composition may then be applied by spraying or other suitable application technique onto a substrate, typically metal or plastic, and cured under ambient conditions.

Typically, the two-component coating composition includes the emulsifier in the same component containing the polyisocyanate composition.
15 Alternatively, the emulsifier may be included in the component containing the isocyanate-reactive resin instead of in the component containing the polyisocyanate. In another option, the aqueous diluent may be separate from the first and second components, and may be contained in a third component, which may also include some of the optional additives. For example, in a three-component composition the
20 emulsifier and isocyanate-reactive resin may be in component one, the polyisocyanate in component two, and an aqueous diluent portion with optional additives in component three. An alternative three-component example the isocyanate-reactive resin may be in component in component one, the emulsifier and polyisocyanate in component two, and an aqueous diluent portion with optional additives in component
25 three.

Aqueous or water dispersible two or three-component coating compositions utilizing the emulsifier of the present invention have excellent properties and performance when cured. These emulsifiers permit polyisocyanates to be readily incorporated into aqueous or water dispersible polymer resins without the
30 need for rigorous agitation.

Examples

This invention is further illustrated by, but is not intended to be limited to, the following examples. All parts and percentages are by weight unless otherwise specified.

5 The following Examples A through E illustrate the preparation of emulsifiers in accordance with the present invention.

Example A

Preparation of an emulsifier

10 A reaction vessel equipped with a stirrer, condenser, temperature probe and nitrogen inlet was charged with 0.36 grams of dibutyltin dilaurate (available from Air Products and Chemicals, Inc.), 120.0 grams (0.50 equivalents) of the isocyanurate of isophorone diisocyanate ("IPDI T-1890" available from Huls America), 60.5 grams dipropylene glycol dimethyl ether solvent ("PROGLYDE DMM" available from the
15 Dow Chemical Company), 60.5 grams methyl ethyl ketone, 40.0 grams (0.05 equivalents) polyethylene glycol monomethyl ether ("CARBOWAX 750 ME" available from Union Carbide Chemicals and Plastics Company) and 200.1 grams (0.45 equivalents) 1-isobutyl isopentyloxy polyethyleneoxyethanol ("SOLVACTANT DMH-7" available from Union Carbide Chemicals and Plastics Company) and heated
20 to 60 to 65°C. The contents of the reaction vessel were stirred until the solid IPDI T-1890 was dissolved. The reaction contents were then heated to 70 to 75°C and stirred until infrared analysis showed no evidence of isocyanate. The resulting product had a total solids content measured at 110°C for one hour of 80.2% by weight, a Brookfield viscosity of 501 centipoise (cps) measured at 60 revolutions per minute (rpm) using a
25 number 4 spindle, and a number average molecular weight of 2252 as determined by gel permeation chromatography utilizing a polystyrene standard.

Example B

Preparation of an emulsifier with optional monoalcohol and amine

A reaction vessel equipped with a stirrer, condenser, temperature probe and nitrogen inlet was charged with 0.55 grams of dibutyltin dilaurate, 240.0 grams (1.0 equivalents) polyisocyanate "IPDI T-1890," 92.1 grams dipropylene glycol dimethyl ether, 92.1 grams methyl ethyl ketone, 80.0 grams (0.11 equivalents) "CARBOWAX 750ME" and 200.1 grams (0.45 equivalents) "SOLVACTANT DMH-7," and heated to 60 to 65°C. The contents of the reaction vessel were stirred until the solid "IPDI T-1890" was dissolved. Then 32.1 (0.45 equivalents) grams diethylamine were added to the reaction, and the contents were stirred until infrared analysis showed no evidence of isocyanate. The resulting product had a total solids content measured at 110 °C for one hour of 78.2% by weight, a Brookfield viscosity of 1010 centipoise (cps) measured at 60 rpm using a number 4 spindle, and a number average molecular weight of 2448 as determined by gel permeation chromatography utilizing a polystyrene standard.

Example C

Preparation of an emulsifier with optional monoalcohol

A reaction vessel equipped with a stirrer, condenser, temperature probe and nitrogen inlet was charged with 0.36 grams of dibutyltin dilaurate, 192.0 grams (0.80 equivalents) polyisocyanate IPDI T-1890, 59.8 grams dipropylene glycol dimethyl ether, 59.8 grams methyl ethyl ketone, 64.0 grams (0.09 equivalents) polyethylene glycol 750 monomethyl ether ("CARBOWAX 750ME" available from the Union Carbide Chemicals and Plastics Company), 102.9 grams (0.71 equivalents) propylene glycol phenyl ether (available as "DOWANOL PPh" from the Dow Chemical Company) and heated to 60 to 65°C. The contents of the reaction vessel were stirred until the solid "IPDI T-1890" was dissolved. The reaction contents were then heated to 70 to 75 °C and stirred until infrared analysis showed no evidence of isocyanate. The resulting product had a total solids content measured at 110°C for

- 10 -

one hour of 75.4% by weight, a Brookfield viscosity of 67,600 centipoise (cps) measured at 12 rpm using a number 5 spindle, and a number average molecular weight of 1335 as determined by gel permeation chromatography utilizing a polystyrene standard.

5

Example D

Preparation of an emulsifier with optional monoalcohol

A reaction vessel equipped with a stirrer, condenser, temperature probe and nitrogen inlet was charged with 0.36 grams of dibutyltin dilaurate, 120.0 grams
10 (0.50 equivalents) polyisocyanate "IPDI T-1890," 60.5 grams dipropylene glycol dimethyl ether, 60.5 grams methyl ethyl ketone, 40.0 grams (0.05 equivalents) "CARBOWAX 750ME," and 202.8 grams (0.45 equivalents) "Igepal CO-530" (nonylphenoxy poly(ethyleneoxy) ethanol available from Rhone-Poulenc) and heated to 60 to 65°C. The contents of the reaction vessel were stirred until the solid "IPDI T-
15 1890" was dissolved. The reaction contents were then heated to 70 to 75°C and stirred until infrared analysis showed no evidence of isocyanate. The resulting product had a total solids content measured at 110°C for one hour of 79.1% by weight, a Brookfield viscosity of 1000 centipoise (cps) measured at 60 rpm using a number 5 spindle, and a number average molecular weight of 2147 as determined by
20 gel permeation chromatography utilizing a polystyrene standard.

Example E

Preparation of an emulsifier with optional monoalcohol

A reaction vessel equipped with a stirrer, condenser, temperature probe
25 and nitrogen inlet was charged with 0.35 grams of dibutyltin dilaurate, 120.0 grams polyisocyanate "IPDI T-1890" (0.50 equivalents), 60.5 grams dipropylene glycol dimethyl ether, 58.4 grams methyl ethyl ketone, 58.4 grams "CARBOWAX 750ME" (0.05 equivalents), and 190.3 grams (0.45 equivalents) "Igepal CA-520" (octylphenoxy poly(ethyleneoxy) ethanol available from Rhone-Poulenc) and heated

- 11 -

to 60 to 65°C. The contents of the reaction vessel were stirred until the solid "IPDI T-1890" was dissolved. The reaction contents were then heated to 70 to 75°C and stirred until infrared analysis showed no evidence of isocyanate. The resulting product had a total solids content measured at 110°C for one hour of 79.1% by weight, a Brookfield viscosity of 1000 centipoise (cps) measured at 60 rpm using a number 5 spindle, and a number average molecular weight of 2147 as determined by gel permeation chromatography utilizing a polystyrene standard.

The following Example F describes an embodiment of acrylic amine polymer that is used as the isocyanate-reactive binder resin in the coating examples set forth herein.

- 12 -

Example F**Preparation of acrylic amine binder**

The following initial charge and feeds were used in the preparation of aqueous secondary amine functional acrylic polymer via solution polymerization

5 technique.

<u>Ingredients</u>	<u>Parts by Weight</u>
<u>Initial Charge</u>	
10 Isopropanol	650.0
<u>Feed 1</u>	
Isopropanol	565.0
n-Butyl acrylate	273.5
15 Methyl methacrylate	783.5
Tert-butylaminoethyl methacrylate	364.5
Styrene	401.0
VAZO-67 ¹	91.0
<u>Feed 2</u>	
20 Acetic acid	88.5
<u>Feed 3</u>	
25 Deionized water	5425.0

¹ 2,2'-Azobis(2-methylbutanenitrile) initiator commercially available from E.I. du Pont de Nemours and Company, Wilmington, Delaware.

30 The initial charge was heated in a reactor with agitation to reflux temperature (81°C). Then Feed 1 was added in a continuous manner over a period of 3 hours. At the completion of Feed 1, the reaction mixture was held at reflux for 3 hours. The resultant acrylic polymer had a total solids content of 59.8 percent determined at 110°C for one hour and number average molecular weight of 4833 as determined by gel

35 permeation chromatography (GPC) using polystyrene as standard.

Following the polymerization, Feed 2 was added over 10 minutes at room temperature with agitation. After the completion of the addition of Feed 2, Feed 3 was added over 15 minutes. Then the reaction mixture was heated for azeotropic

- 13 -

distillation of isopropanol. When the distillation temperature reached 99-100°C, the distillation continued two more hours and then the reaction mixture was cooled to room temperature. The total distillate collected was 2545 grams. After filtration the final aqueous dispersion had a solid content of 31.5 percent and pH of 5.32.

5

Examples 1 through 5 are embodiments of two-component coating compositions in accordance with the present invention. In each of these Examples, Package 1 is an aqueous component containing an isocyanate-reactive polymer, and Package 2 is a polyisocyanate composition containing one of the emulsifiers of Examples A through E. The performance test results of these coatings are set forth in Table I.

EXAMPLE 1

<u>Component</u>	<u>Weight Percent</u>
Package 1	
Acrylic amine of Example F	40.16
Solsperse 27000 ²	0.37
DSX-1514 ³	0.35
Dee Fo 97-3 ⁴	0.11
Exxate 900 ⁵	3.03
n-Propanol ⁶	0.18
Deionized water	20.51
Raven 410 ⁷	0.04
Microtalc MP-12-50 ⁸	9.57
Barimite XF ⁹	9.89
Ti-Pure R902-38 ¹⁰	<u>11.25</u>
Sub Total	95.46
Package 2	
Desmodur N 3200 ¹¹	2.72
Emulsifier of Example A	1.14
Exxate 900	<u>0.68</u>
Sub Total	4.54
Total	100.00

15

² Solsperse® 27000 - Hyperdispersant available from ICI Surfactants, Wilmington, Delaware.

³ DSX-1514 - Thickener available from Henkel, Kankakee, Illinois.

⁴ Dee Fo® 97-3 - Defoamer available from Ultra Additives, Inc., Paterson, New Jersey.

⁵ Exxate® 900 - Solvent available from Exxon Chemical Co., P.O. Box 2180, Houston, Texas.

⁶ n-Propanol - Solvent available from Eastman Chemical Products, Inc., Kingsport, Tennessee.

⁷ Raven® 410 - Carbon black pigment available from Cities Service Co., Columbian Div., Akron, Ohio.

⁸ Microtalc® MP-12-50 - Magnesium silicate hydrate available from Whittaker, Clark, & Daniel Inc., South Plainfield, New Jersey.

⁹ Barimite XF® - Barium sulfate available from Cyprus Industrial Mineral Co., Cartersville, Georgia.

¹⁰ Ti-Pure® R902-38 - Titanium dioxide pigment available from E.I. du Pont de Nemours & Co., Wilmington, Delaware.

¹¹ Desmodur® N 3200 - A hexamethylene diisocyanate biuret available from Miles Inc., Pittsburgh, Pennsylvania.

- 15 -

EXAMPLE 2

<u>Component</u>	<u>Weight Percent</u>
Package 1	
Acrylic amine of Example F	40.16
Solsperse 27000	0.37
DSX-1514	0.35
Dee Fo 97-3	0.11
Exxate 900	3.03
n-Propanol	0.18
Deionized water	20.51
Raven 410	0.04
Microtalc MP-12-50	9.57
Barimite XF	9.89
Ti-Pure R902-38	<u>11.25</u>
Sub Total	95.46
Package 2	
Desmodur N 3200	2.72
Emulsifier of Example B	1.16
Exxate 900	<u>0.66</u>
Sub Total	4.54
Total	100.00

EXAMPLE 3

<u>Component</u>	<u>Weight Percent</u>
Package 1	
Acrylic amine of Example F	40.16
Solsperse 27000	0.37
DSX-1514	0.35
Dee Fo 97-3	0.11
Exxate 900	3.03
n-Propanol	0.18
Deionized water	20.51
Raven 410	0.04
Microcalc MP-12-50	9.57
Barimite XF	9.89
Ti-Pure R902-38	<u>11.25</u>
Sub Total	95.46
Package 2	
Desmodur N 3200	2.72
Emulsifier of Example C	1.21
Exxate 900	<u>0.61</u>
Sub Total	4.54
Total	100.00

EXAMPLE 4

<u>Component</u>	<u>Weight Percent</u>
Package 1	
Acrylic amine of Example F	40.16
Solsperse 27000	0.37
DSX-1514	0.35
Dee Fo 97-3	0.11
Exxate 900	3.03
n-Propanol	0.18
Deionized water	20.51
Raven 410	0.04
Microtalc MP-12-50	9.57
Barimite XF	9.89
Ti-Pure R902-38	<u>11.25</u>
Sub Total	95.46
Package 2	
Desmodur N 3200	2.72
Emulsifier of Example D	1.15
Exxate 900	<u>0.67</u>
Sub Total	4.54
Total	100.00

EXAMPLE 5

<u>Component</u>	<u>Weight Percent</u>
Package 1	
Acrylic amine of Example F	40.16
Solsperse 27000	0.37
DSX-1514	0.35
Dee Fo 97-3	0.11
Exxate 900	3.03
n-Propanol	0.18
Deionized water	20.51
Raven 410	0.04
Microtalc MP-12-50	9.57
Barimite XF	9.89
Ti-Pure R902-38	<u>11.25</u>
Sub Total	95.46
Package 2	
Desmodur N 3200	2.72
Emulsifier of Example E	1.11
Exxate 900	<u>0.71</u>
Sub Total	4.54
Total	100.00

5 Examples 6 and 7 are comparative examples of coatings that do not include the emulsifiers of the present invention. Instead, Example 6 includes a commercially available, water dispersible polyisocyanate in Package 2 that does not require an emulsifier. Although the commercial polyisocyanate of Example 6 yields good coating performance as reported in Table I, it is restricted to the use of a relatively
10 narrow selection of solvents, thus limiting adaptability of formulating coatings, and it requires solvents that make it more difficult to provide the lowest levels of VOC. Example 7 includes a conventional polyisocyanate and no emulsifier.

EXAMPLE 6Comparative - with water dispersible polyisocyanate

<u>Component</u>	<u>Weight Percent</u>
Package 1	
Acrylic amine of Example F	40.30
Solsperse 27000	0.37
DSX-1514	0.35
Dee Fo 97-3	0.11
Exxate 900	3.02
n-Propanol	0.18
Deionized water	20.45
Raven 410	0.04
Microtalc MP-12-50	9.54
Barimite XF	9.86
Ti-Pure R902-38	<u>11.22</u>
Sub Total	95.44
Package 2	
XP-7063 ¹²	3.66
Exxate 900	0.90
Sub Total	<u>4.56</u>
Total	100.00

5 ¹² XP-7063 Water-reducible isocyanate available from Miles Inc., Pittsburgh,
PA.

- 20 -

EXAMPLE 7
Comparative - with no emulsifier

<u>Component</u>	<u>Weight Percent</u>
Package 1	
Acrylic amine of Example F	41.85
Solsperse 27000	0.36
DSX-1514	0.35
Dee Fo 97-3	0.10
Exxate 900	2.98
n-Propanol	0.17
Deionized water	20.19
Raven 410	0.04
Microtalc MP-12-50	9.42
Barimite XF	9.73
Ti-Pure R902-38	<u>11.07</u>
Sub Total	96.27
Package 2	
Desmodur N 3200	2.84
Exxate 900	<u>0.89</u>
Sub Total	3.73
Total	100.00

5

Example 8 illustrates the alternative three component embodiment of the present invention. Example 9 is also a three component coating, but with no emulsifier for comparison purposes.

EXAMPLE 8**Three component coating with emulsifier**

	<u>Component</u>	<u>Weight Percent</u>
5	Package 1	
	Anionic acrylic polyol ¹³	25.30
	Emulsifier of Example A	3.44
	Dibutyl tin diacetate ¹⁴	0.17
10	Tinuvin 384 ¹⁵	1.03
	Tinuvin 123 ¹⁶	0.69
	FC-431 fluorosurfactant ¹⁷	0.07
	Butyl Cellosolve acetate ¹⁸	<u>3.44</u>
	Sub Total	34.14
15	Package 2	
	Cythane 3160 ¹⁹	14.23
	Package 3	
20	Deionized water	<u>51.62</u>
	Total	100.00

25 ¹³ Anionic acrylic polyol is a 70% resin solids, water reducible copolymer supplied in butyl Cellosolve[®] acetate and neutralized with triethylamine. It is composed of 19.0% isobutyl methacrylate, 50.0% butyl acrylate, 6.0% acrylic acid, and 25.0% hydroxyethyl methacrylate.

30 ¹⁴ Dibutyl tin diacetate is available from Air Products and Chemicals Inc., Allentown, Pennsylvania.

¹⁵ Tinuvin[®] 384 is an ultraviolet radiation absorber available from Ciba-Geigy Corp., Hawthorne, New York.

35 ¹⁶ Tinuvin[®] 123 is a hindered amine light stabilizer available from Ciba-Geigy Corp., Hawthorne, New York.

40 ¹⁷ FC-431 is a fluorosurfactant available from 3M Corp., Specialty Chemicals Division, St Paul, Minnesota.

¹⁸ Butyl Cellosolve[®] acetate is ethylene glycol monobutyl ether acetate and is available from Union Carbide Corp., New York, New York.

¹⁹ Cythane® 3160 is an aliphatic polyisocyanate resin supplied by Cytec Industries Inc., Stamford, Connecticut.

EXAMPLE 9

5 **(Comparative three component coating without emulsifier)**

	<u>Component</u>	<u>Weight Percent</u>
	Package 1	
10	Anionic acrylic polyol	28.30
	Dibutyl tin diacetate	0.17
	Tinuvin 384	1.03
	Tinuvin 123	0.69
	FC-431 fluorosurfactant	0.07
15	Butyl Cellosolve acetate	<u>2.24</u>
	Sub Total	32.50
	Package 2	
20	Cythane 3160	15.92
	Package 3	
	Deionized water	<u>51.68</u>
	Total	100.00

25

Test Procedures

Each of the coating formulations of Examples 1-7 was tested for
 30 performance by application onto a substrate prepared as follows:

The coating compositions of the examples were prepared as two-package compositions with the functional acrylic, pigments, and additives in one package (Package 1) and the isocyanate, isocyanate emulsifier, and solvent in a second package (Package 2). In an appropriate grinding vessel, Package 1 was prepared by mixing the
 35 pigments into the resinous vehicle components under high speed agitation with a Cowles blade. After stirring for 5 minutes the Cowles blade was replaced with an Impellar blade, and zircoa beads were then added. This mix was stirred at high speed for 1 hour, after which the beads were separated from the grind paste. The isocyanate package was prepared by blending the isocyanate, isocyanate emulsifier, and solvent in

- 23 -

a separate container, which was hand-shaken until a homogeneous solution resulted. Before spray application, the Package 2 was added to Package 1 with slow and constant agitation.

The substrate for each example was 32 gauge steel panels with a zinc
5 phosphate pretreatment (available from Advanced Coating Technologies, Inc., Hillsdale, Michigan; as cold roll steel B952 P60 DIW, polish) primed with an epoxy-polyamide metal primer, DP-40/DP-401 (a metal primer made by mixing 1 volume DP-40 epoxy primer with 1 volume DP-401 epoxy primer catalyst, both available from PPG Industries, Inc., Pittsburgh, Pennsylvania). The primed substrates were air-dried under
10 ambient conditions for at least 1 hour before the example coatings were applied.

Each blended coating example was applied by air-atomized spray at 45 pounds per square inch over the previously prepared substrates. Each coated substrate was air-dried under ambient conditions for 1 hour. Spray Application was evaluated as follows: good atomization from the spray gun was designated as "pass"; poor paint
15 atomization in which the paint partially clogged the spray gun was designated as "fail." In rating panel appearance, a smooth, continuous film was designated as "pass" and a textured, discontinuous film was designated as "fail."

Each coated panel was dry-sanded with P400 grit sandpaper (P400 - 213Q, Imperial Wetordry® production paper, "A" weight, available from 3M, St. Paul,
20 Minnesota.) Sanded coating that powdered without fouling the sandpaper with grit was designated as "pass." Sanded coating that powdered and fouled the sandpaper with grit was designated as "fail."

Potlife of the example coatings was evaluated as follows: a coating that remained liquid after 1 hour after blending the two components and remained a viscous
25 liquid after 24 hours was designated as "pass." A coating that had liquid with floating oil droplets after 1 hour and a solid crust over liquid after 24 hours was designated as "fail."

TABLE I
COATING PERFORMANCE RESULTS

Example	Spray Application	Panel Appearance	Sanding	Potlife
Example 1	Pass	Pass	Pass	Pass
Example 2	Pass	Pass	Pass	Pass
Example 3	Pass	Pass	Pass	Pass
Example 4	Pass	Pass	Pass	Pass
Example 5	Pass	Pass	Pass	Pass
Example 6	Pass	Pass	Pass	Pass
Example 7	Fail	Fail	Fail	Fail

5

The coating compositions of Examples 8 and 9 were prepared as three package compositions with the polyol, emulsifier, additives and catalyst in Package 1. Package 2 was comprised of the isocyanate crosslinker, and Package 3 was the aqueous diluent. The ingredients of Package 1 were preblended to a homogeneous consistency by mechanical mixing. Package 2 was added to Package 1 immediately before the coating was to be applied and stirred by hand until well mixed. Finally, the water was slowly added to the premixed resin and crosslinker blend with stirring until a sprayable viscosity was obtained and the isocyanate was completely emulsified within the resins.

The preparation of the substrate panels for testing Examples 8 and 9 was similar to Examples 1-7, with the exception that the primed panels were painted with a black acrylic basecoat DBU-9300/DRR-1170 (an acrylic basecoat made by mixing 1 volume of DBU-9300 acrylic basecoat color with 1.5 volumes of DRR-1170 reactive reducer available from PPG Industries, Inc., Pittsburgh, PA). The coatings of Examples 8-9 were applied by air-atomized spray at 50 pounds per square inch over the previously prepared substrates. All results reported in Table II were after 7 days cure at ambient temperature.

TABLE II
COATING PERFORMANCE RESULTS

Example	Gloss	Pencil Hardness	Sward Hardness	Humidity Gloss	Humidity Appearance
Example 8	82	HB	18	81	Good
Example 9	82	HB	16	83	Severe Blushing

5 In Table II, gloss refers to the topcoat gloss and was measured in accordance with ASTM D 523 using a 20 degree gloss meter. Gloss is reported in terms of percent reflected light.

The pencil hardness tests were conducted in accordance with ASTM D 3363. Wood was stripped from pencil of varying hardness, leaving the full
10 diameter of lead exposed to a length of 1/4 inch to 3/8 inch. The end of the lead was flattened at 90 degrees to the pencil axis, and holding the pencil at 45 degrees to the film surface, the pencil is pushed forward about 1/4 inch using as much downward pressure as can be applied without breaking the lead. The result is reported as the highest pencil hardness that produced no rupture of the film. The
15 scale of pencil hardness, from softest to hardest, is as follows:

6B, 5B, 4B, 3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H, 6H, 7H, 8H, 9H, 10H.

Sward Hardness is determined by using a Sward hardness tester available from the Paul N. Gardner Company, Pompano Beach, Florida. The reported values are the number of oscillations of the testing device on the coated surface multiplied by two.
20 A higher Sward number indicates a harder coating.

Humidity refers to humidity testing conducted as per ASTM Method D-2247-68. Humidity results were recorded after a seven day cure at ambient temperature and four days at 100% relative humidity at about 38°C.

The invention has been described in connection with specific
25 embodiments in order to prove the best mode of the invention, but it should be understood that other variations and modifications as are known to those of skill in the art may be resorted to without departing from the scope of the invention as defined by the claims which follow.

We claim:

1. An emulsifier that comprises the reaction product of:
 - (i) an isocyanate and
 - 5 (ii) a member selected from the group consisting of: hydroxy functional polyalkyl ethers containing at least five ethylene oxide groups, alcohols, glycol ethers different from said polyalkyl ethers, amine compounds, and combinations thereof;wherein said hydroxy functional polyalkyl ether is provided in a quantity
10 sufficient to react at least one equivalent of isocyanate groups in isocyanate (i), and the total amounts of reactants (ii) are sufficient to react all of the isocyanate groups of the polyisocyanate (i).
2. The emulsifier of claim 1 wherein the isocyanate (i) is an
15 isocyanurate.
3. The emulsifier of claim 2 where in the isocyanurate is based on isophorone diisocyanate.
- 20 4. The emulsifier of claim 1 wherein reactant (ii) consists essentially of said hydroxy functional polyalkyl ethers containing at least five ethylene oxide groups.
5. The emulsifier of claim 1 wherein reactant (ii) consists
25 essentially of said hydroxy functional polyalkyl ethers containing at least five ethylene oxide groups, and an alcohol or a glycol ether different from said polyalkyl ethers.
6. The emulsifier of claim 1 wherein reactant (ii) comprises: said hydroxy functional polyalkyl ether containing at least five ethylene oxide groups; and an
30 alcohol or a glycol ether different from said polyalkyl ether; and an amine compound.

- 27 -

7. A polyisocyanate composition that is dispersible in water comprising:

(a) a polyisocyanate and

(b) an emulsifier comprising the reaction product of:

5

(i) an isocyanate and

(ii) a member selected from the group consisting of: hydroxy

functional polyalkyl ethers containing at least five ethylene oxide groups, alcohols, glycol ethers different from said polyalkyl ethers, amine compounds, and combinations thereof; said hydroxy functional polyalkyl ether being provided in a quantity sufficient

10 to react at least one equivalent of isocyanate groups in polyisocyanate (i), and the total amounts of reactants (ii) are sufficient to react all of the isocyanate groups of the isocyanate (i).

wherein (b) is present in an amount of from 5 to 75 percent, based on the total weight of (a) and (b).

15

8. The polyisocyanate composition of claim 7 wherein the polyisocyanate (a) is a biuret.

9. The polyisocyanate composition of claim 8 wherein the
20 polyisocyanate (a) is an isocyanurate.

10. The polyisocyanate composition of claim 9 wherein the isocyanurate is based on isophorone diisocyanate.

25 11. The polyisocyanate composition of claim 7 wherein the isocyanate (i) is an isocyanurate.

12. The polyisocyanate composition of claim 11 wherein the isocyanurate is based on isophorone diisocyanate.

30

13. The polyisocyanate composition of claim 7 wherein reactant (ii) consists essentially of said hydroxy functional polyalkyl ethers containing at least five ethylene oxide groups.

5 14. The polyisocyanate composition of claim 7 wherein reactant (ii) consists essentially of said hydroxy functional polyalkyl ethers containing at least five ethylene oxide groups, and an alcohol or a glycol ether different from said polyalkyl ethers.

10 15. The polyisocyanate composition of claim 7 wherein reactant (ii) comprises: said hydroxy functional polyalkyl ether containing at least five ethylene oxide groups; and an alcohol or a glycol ether different from said polyalkyl ether; and an amine compound.

15 16. The polyisocyanate composition of claim 7 wherein the emulsifier (b) is present in an amount of from 15 to 40 percent, based on the total weight of (a) and (b).

20 17. An aqueous two-component coating composition comprising
(I) a polyisocyanate composition comprising:
(a) a polyisocyanate and
(b) an emulsifier comprising the reaction product of:
(i) an isocyanate and
(ii) a member selected from the group consisting of: hydroxy
25 functional polyalkyl ethers containing at least five ethylene oxide groups, alcohols, glycol ethers different from said polyalkyl ethers, amine compounds, and combinations thereof; said hydroxy functional polyalkyl ether being provided in a quantity sufficient to react at least one equivalent of isocyanate groups in polyisocyanate (i), and the total amounts of reactants (ii) are sufficient to react all of the isocyanate groups of the
30 polyisocyanate (i).

- 29 -

wherein the emulsifier (b) is present in an amount of 5 to 75 percent, based on the resin solids weight of (a) and (b); and

(II) an aqueous polymer resin that contains isocyanate-reactive groups, wherein the components I and II are present in an amount sufficient to provide an equivalent ratio of isocyanate groups to isocyanate-reactive groups in II of 0.5:1 to 5:1.

18. The coating composition of claim 17 wherein the polyisocyanate (a) is a biuret.

19. The coating composition of claim 17 wherein the polyisocyanate (a) is an isocyanurate.

20. The coating composition of claim 19 wherein the isocyanurate is based on isophorone diisocyanate.

21. The coating composition of claim 17 wherein reactant (ii) consists essentially of said hydroxy functional polyalkyl ethers containing at least five ethylene oxide groups.

22. The coating composition of claim 17 wherein reactant (ii) consists essentially of said hydroxy functional polyalkyl ethers containing at least five ethylene oxide groups, and an alcohol or a glycol ether different from said polyalkyl ethers.

23. The coating composition of claim 7 wherein reactant (ii) comprises: said hydroxy functional polyalkyl ether containing at least five ethylene oxide groups; and an alcohol or a glycol ether different from said polyalkyl ether; and an amine compound.

- 30 -

24. The coating composition of claim 17 wherein the emulsifier (b) is present in an amount of about 15 to 40 percent based on resin solids weight of (a) and (b).

5 25. The coating composition of claim 17 wherein the aqueous polymer resin (II) is an acrylic polymer having amine functionality.

26. The coating composition of claim 17 wherein the components (I) and (II) are present in an amount sufficient to provide an equivalent ratio of
10 isocyanate groups in (a) to isocyanate-reactive groups in II of about 0.8:1 to 2:1.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/01237

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08G18/28 C08G18/48 C09D175/04 C08G18/79

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 464 781 (MINISTERO DELL UNI E DELLA RIC) 8 January 1992 see page 1, line 56 - page 4, line 4; claims; examples 1,2 ---	1,4,7,13
X	US,A,5 296 160 (TIRPAK ROBIN E ET AL) 22 March 1994 cited in the application see column 2, line 10 - column 6, line 37; examples see column 2, line 26-43 see column 1, line 14-49 ---	1-5, 7-14, 17-22
X	US,A,4 446 256 (HICKS DARRELL D) 1 May 1984 see column 2, line 45 - column 3, line 46; claims 1-9; examples 1-5 --- -/-	1,4,5

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *&* document member of the same patent family

Date of the actual completion of the international search

30 May 1996

Date of mailing of the international search report

11. 07. 96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Hutton, D

INTERNATIONAL SEARCH REPORT

Int. nal Application No
PCT/US 96/01237

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,5 043 381 (COOGAN RICHARD G ET AL) 27 August 1991 see column 4, line 64 - column 5, line 18; claims 1-8; examples ---	1,4-7, 13-15, 17,21-23
X	US,A,4 870 151 (SCHOLL THOMAS ET AL) 26 September 1989 see column 1, line 1 - column 4, line 4; claim 1; examples 1-4 ---	1,4
A	US,A,5 200 489 (JACOBS PATRICIA B ET AL) 6 April 1993 cited in the application see the whole document ---	1-26
A	US,A,3 996 154 (JOHNSON FRANK ET AL) 7 December 1976 see the whole document ---	1,4
A	US,A,5 252 696 (LAAS HANS J ET AL) 12 October 1993 see column 1, line 34 - column 4, line 4 see column 3, line 44 - column 4, line 4; examples -----	1-26

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. l. Application No

PCT/US 96/01237

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0464781	08-01-92	IT-B- 1244866 AT-T- 113626 DE-D- 69104916 DE-T- 69104916	12-09-94 15-11-94 08-12-94 23-03-95
US-A-5296160	22-03-94	AT-T- 129723 CA-A- 2072902 DE-D- 69205745 DE-T- 69205745 EP-A- 0524511 ES-T- 2080994 JP-A- 5214239	15-11-95 24-01-93 07-12-95 11-04-96 27-01-93 16-02-96 24-08-93
US-A-4446256	01-05-84	AU-B- 556879 AU-B- 1714283 CA-A- 1226000 DE-A- 3374688 EP-A,B 0110497 JP-C- 1611112 JP-B- 2038106 JP-A- 59043050	20-11-86 02-02-84 25-08-87 07-01-88 13-06-84 15-07-91 29-08-90 09-03-84
US-A-5043381	27-08-91	CA-A- 1330466 DE-A- 3831170 GB-A- 2209759 JP-A- 1104612	28-06-94 30-03-89 24-05-89 21-04-89
US-A-4870151	26-09-89	DE-A- 3706151 EP-A,B 0281801	08-09-88 14-09-88
US-A-5200489	06-04-93	CA-A- 2082349 CA-A- 2088311	08-05-93 28-08-93
US-A-3996154	07-12-76	GB-A- 1502777 BE-A- 820490 DE-A- 2447135 NL-A- 7412780 SE-A- 7510127	01-03-78 27-03-75 22-04-76 30-03-76 15-03-76
US-A-5252696	12-10-93	DE-A- 4136618	13-05-93

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/01237

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5252696		AT-T- 132515	15-01-96
		CA-A- 2082349	08-05-93
		DE-D- 59204910	15-02-96
		EP-A- 0540985	12-05-93
		ES-T- 2084242	01-05-96
		JP-A- 5222150	31-08-93
		ZA-A- 9208557	05-05-93
